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(54) Title: CRYSTALLINE MULTINARY METAL OXIDE COMPOSITIONS, PROCESS FOR PREPARING AND PROCESSES
FOR USING THE COMPOSITION

(57) Abstract: A new family of crystalline metal oxide compositions have been synthesized. These compositions are described by the empirical formula: $A_nMM'_xM_yO_p$ where A is an alkali metal cation, ammonium ion and mixtures thereof, M is niobium or tantalum, M' is tungsten, molybdenum, or mixtures thereof. M'' is vanadium, tantalum, niobium, titanium, tin, indium, gallium, aluminum, bismuth, antimony, tellurium and mixtures thereof. M'' is an optional metal. These compositions are characterized by having an x-ray diffraction pattern having at least one peak at a d spacing of about 3.9Å. A hydrothermal synthesis procedure as well as hydrocarbon conversion processes using the composition are also disclosed.

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"CRYSTALLINE MULTINARY METAL OXIDE COMPOSITIONS, PROCESS FOR PREPARING AND PROCESSES FOR USING THE COMPOSITION"

BACKGROUND OF THE INVENTION

5 This invention relates to a new family of crystalline metal oxide compositions. These compositions contain either niobium, or tantalum (M), a cation (A) such as an alkali metal, at least one M' metal where M' is tungsten or molybdenum, and optionally a M'' metal such as antimony or vanadium. This invention also relates to a hydrothermal process for preparing the crystalline
10 compositions and to an ammoxidation process using the compositions.

Olefins, e.g., propylene or isobutene are used to prepare a number of higher value products such as aldehydes, acids and nitriles. Since the price of the corresponding alkanes, i.e., propane or isobutane is lower than that of the olefins, it would be advantageous to be able to produce the higher value
15 product directly from the alkanes.

Attempts have been made to synthesize novel materials to catalyze the selective oxidation of paraffins. One such catalyst is described in U.S.-A-5750760 where it is disclosed that a multinary composition having the empirical formula:



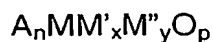
20 where X is an element such as Nb, Ta, W etc. can catalyze the oxidation of an alkane with ammonia in the presence of oxygen. Other compositions which have been disclosed in the art include a $\text{Mo}_4\text{VO}_{14}$ phase by H. Werner et al. in *Catalysis Letters*, **44** (1997) 153-63. In *J. Catalysis* **52**, 116-132 (1978), E.M. Thorsteinson et al., describe a mixed oxide catalyst containing molybdenum
25 and vanadium along with another transition metal such as Ti, Nb, Ta, etc. The authors present activity data and physically characterize the compositions. MoVNb systems have also been described in *Applied Catalysis*, **70** 129-148 (1991) and *Topics in Catalysis* **3**, 355-364 (1996). US-A-4524236 discloses a composition containing molybdenum, vanadium, niobium, antimony plus at
30 least one metal such as lithium, barium, titanium etc. US-A-4339355 discloses a composition comprising $\text{Mo}_a\text{V}_b\text{Nb}_c\text{X}_d$, where X is Co, Cr, Cu, Fe, In, Mn

and/or Y. It is further disclosed that the compositions have spinel or perovskite structures. In US-A-4596787 a catalyst comprising $\text{Mo}_a\text{V}_b\text{Nb}_c\text{Sb}_d\text{X}_e$ is disclosed, where X includes Li, Sc, Na, Fr, Ta, etc. US-A-4250346 discloses a catalyst with an empirical formula of $\text{Mo}_a\text{X}_b\text{Y}_c$, where X is Cr, Mn, Nb, Ta, Ti, V and/or W and Y = Bi, Ce, Co, Cu, Fe, K, Mg, Ni, P, Pb, Sb, Si, Sn, Ti and/or U. US-A-4892856 discloses a catalyst having the composition $\text{Mo}_a\text{V}_b\text{A}_c\text{B}_d\text{C}_e\text{D}_f\text{O}_x$ where A is tungsten or niobium, B is Fe, Cu, Bi, Cr, Sb or Ti, C is an alkali or alkaline earth metal and D is Si, Al or Ti. US-A-5807531 discloses a multimetaloxide having an empirical formula of $\text{Mo}_{12-a-b-c}\text{V}_a\text{M}^1_b\text{M}^2_c\text{O}_x$. However, these materials have a low surface area of $17\text{m}^2/\text{g}$ or lower. Finally, Ueda et al., in *Chem. Commun.*, 1999, 517-518, disclose a Mo-V-M-O (M = Al, Fe, Cr and Ti) composition which is hydrothermally synthesized and in *Applied Catalysis*, 2000, 135-143, disclose Mo-V-M-O (M = Al, Sb, Bi, Te) compositions which are hydrothermally synthesized. Although these compositions have a diffraction peak at about 3.9\AA , they do not have applicant's empirical formula (see below).

In contrast to these reports, applicants have synthesized a new family of crystalline oxide compositions based on either niobium or tantalum, at least one of tungsten and molybdenum, and optionally another metal such as vanadium, antimony or tellurium. These novel compositions are prepared hydrothermally and are characterized in that they have an x-ray diffraction pattern with at least one peak at a d spacing of about 3.9\AA and a high surface area. These materials show good activity for converting propane to acrylonitrile.

SUMMARY OF THE INVENTION

As stated, this invention relates to a new family of crystalline compositions, a process for preparing these compositions and a process which uses the compositions. Accordingly, one embodiment of the invention is a crystalline metal oxide composition having an empirical formula of:



where A is a cation selected from the group consisting of an alkali metal ion, ammonium ion or mixtures thereof, M is tantalum or niobium, M' is

molybdenum, tungsten and mixtures thereof, and M" is selected from the group consisting of antimony, tellurium, vanadium, tantalum, niobium, titanium, tin, indium, gallium, aluminum, bismuth and mixtures thereof, "n" varies from about 0.1 to about 2, "x" varies from about 0.01 to about 8, "y" varies from zero to about 4, and "p" has a value such that it balances the valence of the combined elements, A, M, M', M", the composition characterized in that it has at least one x-ray diffraction peak at a d spacing of about $3.9 \pm 0.15 \text{ \AA}$ and when M is Nb and M' is either Mo or a mixture of W and Mo and M" is V and $y > 0$ then the composition has a surface area of at least $25 \text{ m}^2/\text{g}$ and when M is Nb, M" is not niobium and when M is Ta, M" is not tantalum.

Another embodiment of the invention is a process for preparing the crystalline compositions described above. The process comprising forming a reaction mixture containing reactive sources of A, M, M' and optionally M" at a temperature and a time sufficient to form the crystalline composition, the mixture having a composition expressed in terms of mole ratios of oxides of:

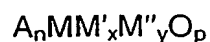


where "a" has a value from about 0.75 to about 4, "b" has a value of about 0.02 to about 10, "c" has a value from 0 to about 5, "q" is the valence of M", and "d" has a value of about 10 to about 500.

These and other embodiments will become clearer after a detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

A new family of crystalline metal oxide compositions has been synthesized and characterized. These compositions contain either niobium or tantalum, at least one of tungsten and molybdenum, and optionally a third metal such as vanadium antimony or tellurium. A cation such as lithium is also present. These crystalline metal oxides are described by the empirical formula:



where "n" varies from 0.1 to 2. The value of "x" varies from 0.01 to 8, while the value of "y" varies from zero to 4. M is niobium or tungsten, M' is molybdenum, tungsten, or mixtures thereof, M'' is selected from the group consisting of vanadium, tantalum, antimony, tellurium, niobium, titanium, tin, indium, aluminum and mixtures thereof. Finally, "p" has a value such that it balances the valence of the combined elements A, M, M', M'' and A is an alkali metal cation, an ammonium cation or mixtures thereof. Examples of the alkali metals which can be used include: lithium, sodium, potassium, rubidium, cesium and mixtures thereof. Of course when M is niobium M' is not niobium and likewise when M is tantalum, M'' is not tantalum.

These novel crystalline metal oxide compositions are hydrothermally prepared. That is, a reaction mixture is prepared from reactive sources of the desired components along with water and heated at a temperature and for a time sufficient to form the desired product. Reactive sources of the alkali metals include the hydroxide, carbonate, halide, acetate, and sulfate compounds. Niobium reactive sources include niobium pentoxide (Nb_2O_5), hydrous niobium oxide, niobium ethoxide, and ammonium niobium oxalate. Molybdenum sources include molybdic acid ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), molybdenum trioxide (MoO_3), sodium molybdate and molybdenum (VI) oxychloride. Tungsten sources include ammonium tungstate, tungsten (VI) oxide, tungsten (VI) chloride, sodium tungstate, and tungstic acid. Vanadium sources include vanadium (V) oxide, vanadium (V) oxychloride, vanadium oxide sulfate, and ammonium vanadate. Tantalum sources include tantalum oxide, hydrous tantalum oxide, tantalum butoxide, tantalum bromide, and tantalum chloride. Tellurium sources include ammonium tellurium oxide, telluric acid, and tellurium oxide. Tin, indium, gallium aluminum and bismuth sources include the nitrates and chlorides, while titanium sources include titanium alkoxides, $(\text{NH}_4)_2\text{Ti}(\text{OH})_2(\text{C}_3\text{H}_4\text{O}_3)_2$ and TiCl_3 . It should be pointed out that this list is only by way of examples and other reactive sources of individual elements may also be used.

Using the above described reactive sources, a reaction mixture is formed which in terms of molar ratios of the oxides is expressed by the formula:



where "a" has a value from about 0.75 to about 4, "b" has a value of about 0.02 to about 10, "c" has a value from 0 to about 5, "q" is the valence of M", and "d" has a value of 10 to 500. Once the reaction mixture is formed, it is required that it have a pH of 4 to 10 and preferably from 6 to 9. This can be done by using a basic compound of the A cation. Alternatively, the A cation can be added as a non-basic compound and the pH adjusted by the addition of an appropriate amount of an organic base such as an alkyl amine or a tetraalkylammonium hydroxide.

Once the reaction mixture is formed and pH adjusted, it is reacted at a temperature of 100-225°C for a period of time of about 1 hr to 96 hr in a sealed reaction vessel under autogenous pressure. After the allotted time, the mixture is filtered to isolate the solid product which is washed with deionized water and dried in air. Alternatively, the product may be isolated and washed by centrifugation techniques. The product may also be washed with aqueous acid rather than deionized water to convert the composition to the proton exchanged form during workup.

The crystalline metal oxide compositions of the invention are characterized by their unique x-ray diffraction pattern and their surface area. The x-ray diffraction pattern has at least one peak at a *d* spacing of $3.9 \pm 0.15 \text{ \AA}$. A second peak at $\frac{1}{2}$ of the $3.9 \pm 0.15 \text{ \AA}$ spacing is also often present in these compositions. Another X-ray diffraction peak, which is sometimes distinct but usually broad, is located at $10.7 \pm 0.25 \text{ \AA}$. This peak is always broader than the 3.9 \AA peak. Diffuse diffraction peaks are also located between 3.42 and 2.98 \AA .

The crystalline metal oxide compositions of the invention are also characterized by their surface areas. These materials generally have a surface area of at least $15 \text{ m}^2/\text{g}$, and preferably at least $25 \text{ m}^2/\text{g}$. When the M metal is niobium and M' is either molybdenum or a combination of molybdenum and tungsten and M" metal is vanadium and $y > 0$, then the surface area must be at

least 25 m²/g. These high surface areas are a result of the instant hydrothermal process.

The above described compositions can be ion exchanged so that the A cation is exchanged for another cation. These cations which can be exchanged into the metal oxide composition (secondary cations) include, without limitation, other alkali metal ions, hydronium ions, alkaline earth ions, lanthanide ions, divalent transition metal ions, trivalent transition metal ions and organic cations such as amphiphilic ammonium ions, quaternary ammonium cations and alkylpyridinium cations. Ion exchange can be carried out by means well known in the art. The process usually involves contacting the composition with a solution containing the desired cation at exchange conditions. Exchange conditions include a temperature of room temperature to 100°C and a time of 20 minutes to 4 days.

The crystalline compositions of this invention can be used in various processes in which hydrocarbons are one of the reactants. Hydrocarbon conversion processes are well known in the art and include cracking, hydrocracking, alkylation of both aromatics and isoparaffin, isomerization, polymerization, reforming, aromatization, hydrogenation, dehydrogenation, transalkylation, dealkylation, hydration, dehydration, hydrotreating, hydrodenitrogenation, hydrodesulfurization, methanation and syngas shift process. Specific reaction conditions and the types of feeds which can be used in these processes are set forth in U.S. Patent Nos. 4,310,440 and 4,440,871 which are incorporated by reference. Preferred hydrocarbon conversion processes are reforming aromatization, transalkylation, isomerization, dealkylation and dehydrogenation. Generally these processes are carried out at a pressure of about 10 to about 750 psig, a weight hourly space velocity of about 0.1 to about 30 hr⁻¹ with respect to the hydrocarbon, a gas hourly space velocity of about 10 to about 10,000 hr⁻¹ with respect to hydrogen and a temperature of about 100°C to about 650°C.

The compositions of this invention can also be used to catalyze transalkylation. By "transalkylation" is meant the process where an alkyl group

on one aromatic nucleus is intermolecularly transferred to a second aromatic nucleus. A preferred transalkylation process is one where one or more alkyl groups of a polyalkylated aromatic compound is transferred to a nonalkylated aromatic compound, and is exemplified by reaction of diisopropylbenzene with
5 benzene to give two molecules of cumene. The reaction conditions for transalkylation include temperatures in the range of about 100° to about 250°C, pressures in the range of 100 to about 750 psig, and a molar ratio of unalkylated aromatic to polyalkylated aromatic in the range from about 1 to about 10.

10 Another process is the ammoxidation of alkanes, such as propane and isobutane to provide nitriles, i.e., acrylonitrile and methacrylonitrile. Conditions for ammoxidation may be found in the art and specifically in US-A- 4788173; 5171876 and 5049692. General conditions include a temperature of 350°C to 700°C, an HSV of 100 to 10,000 hr⁻¹, an ammonia to alkane mole ratio of 0.5:1
15 to 3:1, an oxygen to ammonia mole ratio of 0.5:1 to 10:1 and a pressure of atmospheric to 1034 kPa. The sources of oxygen can be air, pure oxygen or oxygen with a diluent such as nitrogen, etc.

The following examples are set forth in order to more fully illustrate the invention. It is to be understood that the examples are only by way of
20 illustration and are not intended as an undue limitation on the broad scope of the invention as set forth in the appended claims.

EXAMPLE 1

In a mortar there were mixed 1.64 g of Li₂CO₃ and 6.35g of MoO₃ and ground to give a light green powder. To this there were added 6.86 g of
25 Nb₂O₅•12.2H₂O and the combined solids were then ground and added to a beaker containing 14.9g of water. The resulting mixture was mixed, transferred to a PTFE-lined stainless steel reactor and heated under autogenous pressure in an oven at 150°C for 24 hours. This mixture was designated as mixture A1. Similar mixtures were prepared and reacted at various times and temperatures
30 as follows: mixture B1 at 200°C for 24 hours; mixture C1 at 150°C for 48 hours;

mixture D1 at 200°C for 48 hours. After reaction, each product was isolated by centrifugation, washed with water and dried at room temperature.

All four products had substantially similar x-ray diffraction patterns with the main peak at about 3.9Å. Analyses of products B1 and D1 gave respective anhydrous empirical formulas of: $\text{Li}_{0.26}\text{NbMo}_{0.61}\text{O}_p$ and $\text{Li}_{0.33}\text{NbMo}_{0.47}\text{O}_p$. The value of p was not determined in the analysis.

EXAMPLE 2

In a container there were mixed 1.03g of product B1 from example 1 and a solution of 2M nitric acid and the mixture was stirred for 2 days at room temperature. The solid was isolated by filtration, washed with deionized water and dried in a dessicator equipped with calcium sulfate dessicant. Elemental analysis indicated an empirical formula of $\text{NbMo}_{0.55}\text{O}_p \cdot 0.67\text{H}_2\text{O}$. The powder X-ray diffraction pattern displayed higher intensity peaks but the pattern was otherwise unchanged from Product B1 of Example 1.

EXAMPLE 3

A slurry was prepared by mixing in a container 21.8g of $\text{Nb}_2\text{O}_5 \cdot 12.2\text{H}_2\text{O}$ and 91.9g of water followed by the addition of 16.41g of NH_4VO_3 , 49.51g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 4.39g of NH_4OH . The resulting yellow suspension was stirred for 1 hour, divided into aliquots which were placed into PTFE lined steel reactors and reacted as follows: 2A - 150°C for 24 hours, 2B - 150°C for 48 hours, 2C - 200°C for 48 hours; 2E - 225° for 24 hours and 2F - 225°C for 48 hours. The reactor products were isolated by centrifugation and washed with 200 ml of 1M HNO_3 . Elemental analysis of sample 2A gave an empirical formula, expressed as anhydrous oxide, of $\text{NbV}_{0.23}\text{Mo}_{0.8}\text{O}_p$. The x-ray diffraction pattern of sample 2B and sample 2C were essentially identical to those of example 1, while the other samples showed the presence of impurities.

EXAMPLE 4

A series of compositions were prepared as described above and a description of the reaction mixture, synthesis conditions and empirical formulas

are presented in Table 1. In each case, the major product was one displaying an x-ray powder diffraction pattern with peaks at about 3.91Å, 1.96Å and a peak at about 10.8Å with varying degrees of broadness and definition.

TABLE 1

SUMMARY OF PREPARATION OF VARIOUS COMPOSITIONS

Sample I.D.	Empirical Formula of Product (p not determined in analysis)	Reaction Mixture	Conditions	BET m ² /g
4A	Li _{0.5} NbV _{0.23} Mo _{1.22} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.50V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs 150C	
4B	Li _{0.53} NbV _{0.24} Mo _{1.52} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.50V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs 200C	32
4C	Li _{0.52} NbV _{0.3} Mo _{1.38} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.50V ₂ O ₅ -2MoO ₃ -45H ₂ O	48hrs 150C	56
4D	Li _{0.45} NbV _{0.21} Mo _{1.3} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.50V ₂ O ₅ -2MoO ₃ -45H ₂ O	48hrs 200C	
4E	Li _{0.44} NbV _{0.15} Mo _{1.03} O _p	Li ₂ O-0.48Nb ₂ O ₅ -0.25V ₂ O ₅ -2MoO ₃ -47.5H ₂ O	48hrs 150C	166
4F	Li _{0.34} NbV _{0.12} Mo _{0.8} O _p	Li ₂ O-0.48Nb ₂ O ₅ -0.25V ₂ O ₅ -2MoO ₃ -47.5H ₂ O	48hrs 200C	132
4G	Na _{0.38} NbMo _{0.8} O _p	Na ₂ O-0.64Nb ₂ O ₅ -2MoO ₃ -50H ₂ O	24hrs 150C	105
4H	Na _{0.31} NbMo _{0.5} O _p	Na ₂ O-0.64Nb ₂ O ₅ -2MoO ₃ -50H ₂ O	24hrs 200C	95
4I	Li _{0.5} NbV _{0.3} Mo _{1.49} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs 150C	
4J	Li _{0.96} NbV _{1.38} Mo _{1.93} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs 200C	41
4K	Li _{1.27} NbV _{1.91} Mo _{2.1} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs 225C	48
4L	Li _{0.58} NbV _{0.3} Mo _{1.66} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	48hrs 150C	86
4M	Li _{1.26} NbV _{1.87} Mo _{2.26} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	48hrs 200C	41
4N	Li _{1.78} NbV _{2.13} Mo _{2.64} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.75V ₂ O ₅ -2MoO ₃ -45H ₂ O	48hrs 225C	29
4O	Li _{0.53} NbV _{0.26} Sb _{0.35} Mo _{1.34} O _p	Li ₂ O-0.26Nb ₂ O ₅ -0.5V ₂ O ₅ -0.10Sb ₂ O ₅ -2MoO ₃ -44H ₂ O	24hrs 225C	78
4P	Li _{0.83} NbV _{0.19} Sb _{0.2} Mo _{1.32} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.25Sb ₂ O ₅ -0.25V ₂ O ₅ -2MoO ₃ -45H ₂ O	24hrs @ 150C	
4Q	NbMo _{1.1} V _{0.2} Sb _{1.05} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.5V ₂ O ₅ -0.25Sb ₂ O ₄ -2MoO ₃ -45H ₂ O	72 hrs. @ 150C*	150
4R	NbMo _{1.3} V _{0.48} Sb _{0.66} O _p	Li ₂ O-0.32Nb ₂ O ₅ -0.5V ₂ O ₅ -0.25Sb ₂ O ₄ -2MoO ₃ -45H ₂ O	72 hrs. @ 200C*	113

* washed with aqueous HNO₃

EXAMPLE 5

Several of the compositions described in examples 1-4 were tested in a continuous flow fixed bed laboratory plant. The reactor consisted of a ¾" ID stainless steel tube reactor which contained a 10 cc catalyst bed volume. The propane, ammonia, air and nitrogen (diluent) were mixed at the top of the reactor and down flowed over the catalyst. The amount of catalyst in the bed can be varied from 2 cc to 10 cc with the remainder of the volume being taken up with inert quartz sand. The catalyst tests were carried out at the temperatures indicated in Table 2, and the effluent was analyzed by GC. Results of these tests are presented in Table 2.

TABLE 2

LABORATORY ACTIVITY RESULTS FOR SELECTED CATALYSTS

Catalyst I.D.	Cat. Vol. (cc)	C ₃ /NH ₃ /O ₂	Flow Rate (cc/min)	Vol % C ₃	Test Temp. °C	C ₃ Conv. (%)	ACN Selectivity (%)
4Q	2.5	1/1.2/1.6	117	7.5	440	24	25
4R	2.0	1/1.2/1.6	117	7.5	417	19	18

The results in Table 2 show that the compositions of this invention can convert propane and selectively make acrylonitrile (ACN).

EXAMPLE 6

Into a mortar there were placed 1.64g of Li₂CO₃ and 5.18g, WO₃ which were ground together. To this there were added 3.56g Nb₂O₅•12.2H₂O and the mixture ground well to give a damp yellow-green powder. This powder was added to a beaker containing 15.33 g of water, stirred for 1 hour, placed in a PTFE lined stainless steel reactor and heated under autogenous pressure in an oven for 168 hours at 150°C.

The solid product from this reaction was isolated by centrifugation, washed 3 times with about 200 ml of deionized water and dried at 100°C. Elemental analysis revealed the presence of 1.12% Li, 30.1% Nb, 42.9% W

with an LOI of 5.87 mass %, giving a product formula of $\text{Li}_{0.50}\text{NbW}_{0.73}\text{O}_p \cdot 0.19\text{H}_2\text{O}$. X-ray powder diffraction revealed peaks at 3.91 and 1.96 Å, and a poorly defined broad peak at about 10.8 Å.

EXAMPLE 7

- 5 In a mortar, 1.80 g Li_2CO_3 was ground, followed by the addition of 10.25 g WO_3 and further grinding. Next, 6.90g $\text{Nb}_2\text{O}_5 \cdot 12.2\text{H}_2\text{O}$ was added and the mixture was ground to yield a damp yellow-green powder. This powder was then added to a vessel containing 15.2 g of water and stirred for 1 hour after which the pH was 8.31. The resultant mixture was loaded into a PTFE lined stainless steel
- 10 reactor and reacted for 48 hours at 200°C. After the reaction was completed, the solid reaction products were isolated by high-speed centrifugation. After centrifugation, the supernatant solution appeared to be colloidal and was decanted and retained as fines. The solids isolated by initial centrifugation were washed three times with 150 ml of deionized water and isolated by
- 15 centrifugation. Each wash yielded colloidal supernatants that were decanted into the fines sample. The centrifuged supernatant containing the fines was then evaporated to dryness in a 100°C forced air oven. X-ray powder diffraction patterns were characterized by the following data:

TABLE 3

XRD Powder Diffraction Data for Course (fines) Products

2-theta	d (Å)	I
Course (fines)	Course (fines)	Course (fines)
~8, (8.5)	~11, (10.39)	Poorly defined (Medium, broad)
22.72 (22.72)	3.91, (3.91)	Strong, (strong)
46.42 (46.32)	1.95, (1.95)	Weak (weak)

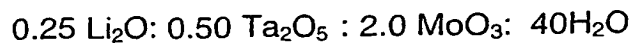
Elemental analysis of the course and fines products revealed the following, in wt. %:

- 5 Course product: 1.20% Li, 22.9% Nb, 52.9% W with an LOI of 9.89 mass %, giving the empirical formula $\text{Li}_{0.7}\text{NbW}_{1.17}\text{O}_p$.

Fines product: 1.99% Li, 25.6% Nb, 46.1% W with an LOI of 9.97 mass %, giving the empirical formula $\text{Li}_{1.04}\text{NbW}_{0.92}\text{O}_p$.

EXAMPLE 8

- 10 Amorphous hydrous Ta_2O_5 was prepared by adding 34.0 g of $\text{TaCl}_5 \cdot n\text{H}_2\text{O}$ to 2000 g of deionized water. The pH of this mixture was adjusted to 10.37 using 147.0 g of concentrated NH_4OH which gave a precipitate which was isolated by filtration. The solid precipitate was washed with 2000 ml of deionized water and partially dried. A reaction mixture was prepared by
- 15 suspending 27.04 g $\text{Ta}_2\text{O}_5 \cdot 13\text{H}_2\text{O}$, prepared above, in 48.3 g of deionized water and adding to it a homogeneous powder of 1.50 g Li_2CO_3 and 23.03 g MoO_3 . The resultant reaction mixture was stirred for one hour and was found to have a pH of 5.02 and a composition in terms of molar oxide ratios of;



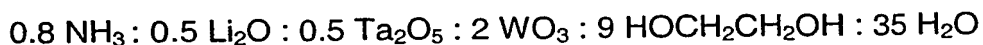
The reaction mixture was divided into 4 portions and reacted under autogenous pressure for 24 and 72 hours at either 200°C or 225°C. The solid product from each reaction was isolated by centrifugation, washed and then dried at 100°C. The product from the 72 hour at 225°C reaction was found to have an intense x-ray diffraction peak at a *d*-spacing of about 3.95 Å. Elemental analysis showed that the product had an empirical formula of:



The N₂ BET surface area was determined to be 141 m²/g. This product was identified as sample A.

EXAMPLE 9

Into a container there were placed 42.6 g of a solution prepared by dissolving 13.1 g of LiCl in 50.4 g deionized water. To this solution there were added 29.1 g of an aqueous solution formed by dissolving 20.7 g of (NH₄)₆W₁₂O₃₉ : nH₂O in 25.3 g of deionized water. To the resultant clear solution there were added 107.1 g of a solution prepared by mixing 32.7 g Ta(OC₂H₅)₅ in 150.1 g ethylene glycol. After addition of the tantalum solution, the mixture was stirred vigorously and found to have a pH of 4.42. The pH was adjusted to 6.44 by adding 1.0 g of concentrated ammonium hydroxide while stirring. The reaction mixture was found to have a composition of:



After stirring the reaction mixture for one hour, it was split into 6 aliquots, loaded into Teflon lined reactors and reacted under autogenous pressure at 200°C and 225°C for periods of 3, 7 and 14 days. At the end of the reaction times, the reactors were cooled to room temperature where the solid products were isolated by vacuum filtration, washed and then dried. X-ray diffraction analysis of the samples revealed the presence of diffraction peaks at about 3.9Å, but also contained about 10-20% of a pyrochlore-type impurity. Elemental analysis showed that the above products have an empirical formula expressed as the ratio of the oxides of :

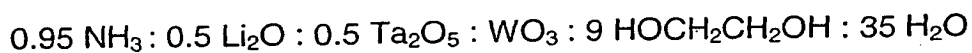
Elemental Analysis for Li-Ta-W-O materials

Sample ID	Crystallization Conditions	Product Formula
B	72 hours at 200°C	Li _{0.25} Ta W _{1.56} O _{7.29} : 4.33 H ₂ O
C	168 hours at 200°C	Li _{0.22} Ta W _{1.62} O _{7.46} : 3.71 H ₂ O
D	336 hours at 225°C	Li _{0.23} Ta W _{1.67} O _{7.62} : 11.17 H ₂ O

Nitrogen BET surface area was found to be 87 m²/g for Sample D.

EXAMPLE 10

In a beaker there were placed 47.8 g of a solution prepared by dissolving
 5 13.1 g LiCl in 50.1 g distilled water. To this solution there were added 35.2 g of
 a solution prepared by dissolving 12.45 g of (NH₄)₆W₁₂O₃₉ : nH₂O in 25.3 g of
 distilled water. To the resulting clear solution there were added 179 g of a
 solution prepared by mixing 37.2 g of Ta(OEt)₅ in 150.6 g of ethylene glycol. To
 the creamy gel which formed, 60 g of distilled water were added followed by
 10 10.84 g of concentrated NH₄OH in order to adjust the pH from 4.54 to 6.8. The
 reaction mixture was found to have the following composition:



The mixture was stirred for 1 hour and then divided into 9 aliquots which
 were loaded in to Teflon lined reactors and the mixtures reacted for 1, 5 and 7
 15 days at 150°C, 200°C and 225°C. At the end of the reaction times, the solid
 products were isolated by vacuum filtration, washed and dried in air. Elemental
 analysis showed the solid product to have a composition expressed by the
 formulas:

Sample ID	Crystallization Conditions	Product Formula
E	72 hours at 150°C	$\text{Li}_{0.01} \text{Ta W}_{0.37} \text{O}_{3.69} : 1.75 \text{H}_2\text{O}$
F	72 hours at 200°C	$\text{Li}_{0.00} \text{Ta W}_{0.37} \text{O}_{3.59} : 2.95 \text{H}_2\text{O}$
G	72 hours at 225°C	$\text{Li}_{0.00} \text{Ta W}_{0.37} \text{O}_{3.59} : 2.52 \text{H}_2\text{O}$

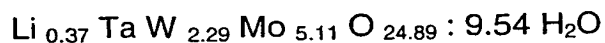
EXAMPLE 11

In a beaker, there were added 55.8 g of an aqueous solution having the composition $\text{LiCl} : 9\text{H}_2\text{O}$ and to it there were added 183.5 g of an aqueous solution having the composition $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} : 196 \text{H}_2\text{O}$ to give a clear solution to which there were added 41.0 g of an aqueous solution having the composition $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} : 200 \text{H}_2\text{O}$ to give a clear solution. Finally, 63.0 g of a solution having a composition $\text{Ta}(\text{OC}_2\text{H}_5)_5 : 30$ ethylene glycol was added which resulted in a thin white gel having a pH of 5.63.

The composition of the reaction mixture in terms of molar oxide ratios was determined to be:



After stirring the mixture for 1 hour, it was split into several aliquots, loaded into Teflon lined reactors and the mixtures reacted either quiescent or tumbled (in an oven equipped with a rotisserie rack) at 150°C and 200°C for various times. When the reaction times were completed, the solid products were isolated by vacuum filtration, washed and then dried in ambient air. The solid reaction product which was reacted with tumbling for 72 hours for 150°C was found to have a x-ray diffraction peak at a d -spacing of 3.91Å. Elemental analysis was carried out on this product and found to have a composition described by the empirical formula of:



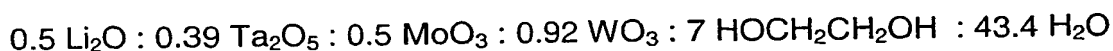
Nitrogen BET surface area for the sample was found to be 70 m²/g. This product was identified as sample H.

A 3.5 g portion of the solid product obtained above was slurried in 200 mL of 1M HNO₃ for 2 hours at room temperature, vacuum filtered to isolate the solid product and then washed with 500 mL 1 M HNO₃. This product was identified as Sample I.

EXAMPLE 12

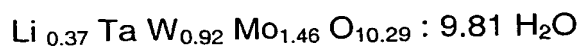
Into a beaker there were added 20.7 g of an aqueous solution having the composition LiCl : 9H₂O to which 34.0 g of an aqueous solution having the composition (NH₄)₆Mo₇O₂₄ : 196 H₂O was added. To the resultant clear solution, 13.9 g of an aqueous solution having the composition (NH₄)₆W₁₂O₃₉ : 200 H₂O were added followed by the addition of 60.0 g of a solution having the composition Ta(OC₂H₅)₅ : 30 ethylene glycol to give a thin white gel having a pH of 6.24.

The composition of the reaction mixture in terms of molar oxide ratios was found to be:



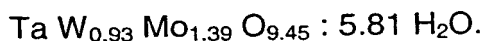
The mixture was stirred for an hour, split into several aliquots which were loaded into Teflon lined reactors and the mixtures reacted at either 150°C or 200°C for various times under quiescent autogenous conditions. At the completion of the reaction times, the solid products were isolated by vacuum filtration, washed and then dried at ambient air.

The solid product obtained after 72 hours at 150°C with tumbling was found to have a x-ray diffraction peak at 3.84Å. Elemental analysis of this product gave a composition having the empirical formula of:



Nitrogen BET surface area was measured to be 145 m²/g. This product was identified as sample J.

A 3.5 g portion of the solid product obtained above was slurried in 200 mL of 1M HNO₃ for 2 hours at room temperature, vacuum filtered to isolate the solid product and then washed with 500 mL 1 M HNO₃. After drying, elemental analysis showed that this product contained less than 0.002 wt. % Li and gave a composition with the empirical formula of:



Nitrogen BET surface area was found to be 125 m²/g. This product was identified as product K.

EXAMPLE 13

To 292 g of an aqueous solution having the composition LiCl:9H₂O there were added 509.7 g of an aqueous solution having the composition (NH₄)₆Mo₇O₂₄ : 196 H₂O, followed by the addition of 153.7 g of an aqueous solution having the composition (NH₄)₆W₁₂O₃₉ : 200 H₂O. Finally, 744.0 g of a solution having the composition 0.27 Ta(OC₂H₅)₅ : 0.75 Nb(OC₂H₅)₅ : 30 ethylene glycol was added and a thin white gel having a pH 6.07 formed.

The composition of the reaction mixture in terms of molar oxide ratios was found to be:



A 436.8 g portion of this reaction mixture was loaded into a Teflon lined stirred reactor and the mixture reacted for 8 hours at 150°C. After cooling to room temperature, the solid product was isolated by vacuum filtration, washed and then dried at ambient air. Elemental analysis of the product gave a composition having an empirical formula of:



Nitrogen BET surface area was measured to be 161 m²/g. This product was identified as Sample L. A 3.5 g portion of Sample L was slurried in 200 mL of 1M HNO₃ for 2 hours at room temperature, vacuum filtered to isolate the solid

product and then washed with 500 mL 1 M HNO₃. This product was identified as sample M.

EXAMPLE 14

Samples from Examples 1, 2, 3 and 6 were tested for the
 5 dehydrogenation of methylcyclohexane (MCH) to toluene using the following
 procedure. In a reactor there were placed 250 mg (40-60 mesh) of the sample
 to be tested and the sample was pretreated at 565°C for 180 min. in hydrogen.
 The sample was then cooled to 300°C under hydrogen. Over this sample there
 was flowed, at a rate of 250 cc/min, methylcyclohexane that was saturated with
 10 hydrogen at 0°C. The temperature was then increased and measurements
 taken at 300°C, 325°C, 350°C, 375°C, 400°C, 450°C and 500°C. Analysis of
 the effluent was carried out using a GC analyzer. The results of these
 experiments are shown in Table 1.

TABLE 4

15 Methylcyclohexane Conversion for Various Compositions

Sample ID	Conversion at Stated Temperature						
	300°C	325°C	350°C	375°C	400°C	450°C	500°C
A	4.89	9.07	15.05	21.67	29.7	49.4	68.9
B	0.97	1.56	2.31	3.08	4.18	8.88	17.9
C	1.05	1.65	2.33	3.75	3.97	8.66	17.5
D	5.23	7.29	9.42	11.1	13.6	22.9	35.1
F	0.87	1.18	1.35	1.57	1.97	3.79	6.74
L	3.51	6.40	10.05	12.45	13.87	20.71	34.19

Analysis of the products obtained at 500°C is shown in Table 2.

TABLE 5
Product Distribution (%) of Various Compositions at 500°C

Sample ID	Benzene	Cyclohexane	MCH	Toluene	Unknowns
A	2.53	0	31.13	64.01	0.59
B	0.53	0	82.13	15.09	0.91
C	0.45	0	82.55	14.84	0.83
D	6.76	0	64.94	30.74	0.87
F	0.12	0	93.26	5.14	0.88
L	0.69	0	65.81	31.47	0.67

The results in Tables 1 and 2 show that the compositions of this invention have good dehydrogenation activity.

5

EXAMPLE 15

Several samples were tested for heptane cracking using the following test procedure. In a reactor there were placed 250 mg (40-60 mesh) of a given sample and the sample was pretreated at 400°C for 1 hour under hydrogen and then cooled to 350°C. Over this sample there was flowed, at a rate of 125 cc/min., a feedstream of n-heptane that was saturated with hydrogen at 0°C. The temperature was then raised and measurements taken at 350°C, 400°C, 450°C and 500°C. Analysis of the effluent was carried out using a GC analyzer. Conversion at various temperatures is shown in Table 3.

TABLE 6
Heptane Conversion vs. Temperature for Various Compositions

Sample ID	Conversion (%) at stated Temperature			
	300°C	350°C	400°C	500°C
B	0.60	0.56	0.55	3.89
C	0.51	0.55	0.65	4.03
D	0.54	1.02	3.25	18.71
H	6.56	21.12	23.43	24.25
I	13.79	22.4	24.47	31.97
J	0.47	0.5	0.78	5.77
K	8.7	17.42	16.84	17.87
L	0.66	1.56	3.17	11.39
M	9.37	15.56	14.95	17.83

Analysis of the products produced at 500°C are presented in Table 4.

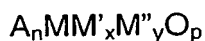
TABLE 7
Product Distribution (%) of Various
Compositions at 500°C

Sample ID	Aromatics	Isomerized products	Napthenes	Cracking	Unknowns
B	0.24	1.45	0.61	1.44	0.15
C	0.28	1.41	0.64	1.54	0.16
D	5.59	0.81	0.76	8.41	3.14
H	10.17	1.72	1.37	9.98	1.01
I	18.04	1.46	0.82	11.66	0
J	1.63	1.35	1.33	1.44	0.03
K	8.05	2.19	1.17	6.38	0.08
L	4.71	1.41	1.62	3.66	0
M	8.31	1.51	0.99	7.02	0

The data in Table 4 show that the compositions of this invention have significant acidity, can isomerize paraffins and aromatize n-heptane.

CLAIMS:

1. A crystalline metal oxide composition having an empirical formula of:



where A is a cation selected from the group consisting of an alkali metal ion, ammonium ion or mixtures thereof, M is tantalum or niobium, M' is molybdenum, tungsten and mixtures thereof, M'' is selected from the group consisting of vanadium, tantalum, antimony, tellurium, niobium, titanium, tin, indium, gallium, aluminum, bismuth and mixtures thereof, "n" varies from about 0.1 to about 2, "x" varies from about 0.01 to about 8, "y" varies from zero to about 8, and "p" has a value such that it balances the valence of the combined elements, A, M, M', M'', the composition characterized in that it has at least one x-ray diffraction peak at a d spacing of about $3.9 \pm 0.15 \text{ \AA}$ and when M is Nb and M' is either Mo or a mixture of W and Mo and M'' is V and $y > 0$ then the composition has a surface area of at least $25 \text{ m}^2/\text{g}$ and when M is Nb, M'' is not niobium and when M is Ta, M'' is not tantalum.

2. The composition of claim 1 where A is lithium.
3. The composition of any of claims 1 or 2 where M' is molybdenum.
4. The composition of any of claims 1 to 3 further characterized in that the A cation has been exchanged for a secondary cation selected from the group consisting of hydronium ions, alkali ions, alkaline earth ions, lanthanide ions, divalent transition metal ions, trivalent transition metal ions, organic cations and mixtures thereof.
5. A process for preparing a crystalline metal oxide composition having an empirical formula of:



where A is a cation selected from the group consisting of an alkali metal ion, an ammonium ion or mixtures thereof, M is tantalum or niobium, M' is molybdenum, tungsten or mixtures thereof, M'' is selected from the group

consisting of vanadium, antimony, tellurium, niobium, titanium, tin, indium, gallium, aluminum, bismuth, tantalum and mixtures thereof, "n" varies from about 0.1 to about 2, "x" varies from about 0.01 to about 8, "y" varies from zero to about 8, and "p" has a value such that it balances the valence of the combined elements, A, M, M', M", the composition characterized in that it has at least one x-ray diffraction peak at a d spacing of about $3.9 \pm 0.15 \text{ \AA}$ and when M is Nb and M' is either Mo or a mixture of W and Mo and M" is V and $y > 0$ then the composition has a surface area of at least $25 \text{ m}^2/\text{g}$ and when M is Nb, M" is not niobium and when M is Ta, M" is not tantalum. The process comprising forming a reaction mixture containing reactive sources of A, M, M' and optionally M" at a temperature and a time sufficient to form the crystalline composition, the mixture having a composition expressed in terms of mole ratios of oxides of:



where "a" has a value from about 0.75 to about 4, "b" has a value of about 0.02 to about 10, "c" has a value from 0 to about 5, "q" is the valence of M", and "d" has a value of about 10 to about 500.

6. The process of claim 5 where the temperature varies from about 100°C to about 225°C and the time varies from about 1 hour to about 96 hours.

7. The process of claim 5 further characterized in that the A cation is exchanged for a secondary cation selected from the group consisting of hydronium ions, alkali ions, alkaline earth ions, lanthanide ions, divalent transition metal ions, trivalent transition metal ions, organic cations and mixtures thereof by contacting the composition with solution containing at least one of said secondary cation at exchange conditions thereby exchanging the A cation for the secondary cation.

8. A hydrocarbon conversion process comprising contacting a hydrocarbon with a catalyst at hydrocarbon conversion conditions to give a hydroconverted product, where the catalyst comprises the composition of any of claims 1 to 4.

9. The process of claim 8 where the hydrocarbon conversion process is selected from the group consisting of ammoxidation, aromatization, dehydrogenation, isomerization, reforming and transkylation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/35011**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :B01J 21/00, 23/00; C07C 5/00

US CL :502/311, 312; 585/658

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/311, 312; 585/658

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST Image search**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,524,236 A (MCCAIN) 18 June 1985, cols. 2-3.	1-9
X	US 4,892,856 A (KAWAJIRI et al) 09 January 1990, abstract.	1-9
X	US 6,043,185 A (CIRJAK et al) 28 March 2000, abstract.	1-9
X	US 6,037,304 A (ABDULWAHED et al) 14 March 2000, cols. 2,3.	1-9
X,E	US 6,171,571 B1 (BEDARD et al) 09 January 2001, col. 2.	1-9

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 MARCH 2001

Date of mailing of the international search report

26 APR 2001

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